REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

2

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
		Reprint

4. TITLE AND SUBTITLE
Title shown on Reprint

5. FUNDING NUMBERS
DAAL03-87-C-0016

6. AUTHOR(S)
Authors listed on Reprint

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Texas Instruments, Inc.
Dallas, TX 75265

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
ARO 25285.2-MS-A

11. SUPPLEMENTARY NOTES
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

ABSTRACT SHOWN ON REPRINT

14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500
Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

INTELLIGENT PROCESSING OF MATERIALS

Proceedings of a symposium sponsored by the Process Control Committee of the Materials Design and Manufacturing Division, held at the Fall Meeting of The Minerals, Metals & Materials Society in Indianapolis, Indiana, October 2-5, 1989.

Edited by

Haydn N. G. Wadley
University of Virginia
Charlottesville, Virginia

W. Eugene Eckhart, Jr.
U.S. Department of Energy
Washington, D.C.

A publication of
TMS
Minerals • Metals • Materials

Ref.
pp 91-120

INTELLIGENT GROWTH OF HgCdTe

BY THE TRAVELING HEATER METHOD

David E. Witter
Texas Instruments, Inc.
13532 North Central Expressway
Dallas, Texas 75243

ABSTRACT

Large single crystals of (Hg,Cd)Te with desired materials characteristics including radial uniformity of composition and minimal concentrations of defects have been grown from excess tellurium solutions in high purity quartz ampoules by the Traveling Heater Method. Successful transfer of this technology from the laboratory to production requires the implementation of better process controls primarily for improved axial uniformity of composition. Model based predictive control of the crystal growth process is anticipated with the necessary sensors have been applied to this multivariable problem. Eddy Current analysis of the solvent volume and interface shapes, capacitance manometry of mercury partial pressures, precision fiber optic thermometry of thermal gradients and nuclear gauges of composition will be discussed. A computational fluid dynamic and thermodynamic model of mass and thermal transport is proposed.

Introduction

Statement of Need

A rapidly increasing demand exists for weapon systems that utilize infrared techniques for target acquisition, terminal guidance, tracking, night vision enhancement, and numerous other applications. Texas Instruments Incorporated (TI) currently is participating in programs for full scale development (FSD) of the Commanders Independent Thermal Viewer (CITV), a night vision system for installation on the M1 tank, and the Anti-Armor Weapon System-Medium (AAWS-M), a fire and forget infrared guided missile for top attack scenarios against tanks. Large scale production is scheduled to begin in 1991 for the CITV and in 1993 for AAWS-M. TI has or anticipates receiving follow on contracts for infrared sensors and weapons systems requiring large scale production generally starting in 1995.

Program Benefits and Goals

The benefit of the successful completion of the "Intelligent Growth of (Hg,Cd)Te" program will be the implementation of an economical production process for the focal plane arrays (FPAs) used in these weapon systems. The first program phase emphasizes the mercury cadmium telluride (HgCdTe) detector material with the following goals and benefits:

- Models that accurately predict the growth process
- Sensors that monitor critical growth parameters
- Controls that optimize material quality on real time basis during growth
- Optimized material characteristics, including compositional uniformity over an entire ingot, stress free and low defect material, and large, single crystals of 25 mm diameter x 50 mm length
- Routine growth of HgCdTe compatible with high volume FPA needs.

Focal Plane Status, Issues, and Problems

The critical element in the producibility of these systems is the infrared focal plane array (FPA). These arrays have evolved from those already fielded in the DoD common module FLIR systems and represent the next generation in performance capability required for this expanding application base. In comparison to the common module detector, these arrays have many times the number of individual elements. This gives increased sensitivity and/or increased field or view capability to the incorporating systems. The price paid for these improvements in increased detector complexity is manifested in the array fabrication procedure and more stringent requirements on the detector material.

The focal planes now in development at TI are based on a Vertically Integrated Metal-Insulator-Semiconductor (VIMIS) architecture. The elements are photocapacitors as opposed to the common module photoconductors and offer the advantages of reduced power consumption and significant on-focal-plane signal processing. These advantages are critical factors for accommodating the applications driven increase in number of detector elements on the focal plane.

The overriding problem in building these arrays is establishing the specified performance levels required by the high performance systems. There is a major emphasis now being placed on understanding this problem. Areas of analysis and experimentation include: 1/F

and white noise, process variables, and HgCdTe detector material. This becomes a very complex and difficult problem to address because of the interrelationship between the as grown material properties and the impact on these properties during device processing. Undoubtedly, the major area of concern is the inability to consistently produce the very high quality detector material needed for these arrays.

Material Requirements and Issues

The material requirements for the focal plane arrays are more stringent than those for the photoconductors. There are two reasons for this. First, these detectors are operated under electrical biasing conditions such that regions of high electric field exist near the surface of the detector. These fields can couple with defects in the material and create dark current which can mask signal currents. Even in material with no physical defects these fields can create excessive dark current unless the material is very pure. The biasing conditions then require the material to be specified according to parameters such as dislocation density and degree of donor and acceptor compensation. The second burden that these FPA materials must bear is one of increasing array size. The material specifications must now hold over much larger spatial extent. The 960 X 4 Alicat array has dimensions of 0.72" x 0.075", a 7-fold increase over the photoconductive arrays used in common modules.

Material requirements are listed in Table 1. These requirements represent a significant challenge for the material growth process. The solid state recrystalization (SSR) growth technique now used in production has been able to meet these requirements but with very low yield.

TABLE 1. MATERIAL REQUIREMENTS FOR LWIR FOCAL PLANE ARRAYS

PARAMETERS	SPECIFICATIONS
Electrical Type at 77K	N-Type
Preferred Orientations	(111)B, (112), or (113)
N_D-N_A at 77K (cm^{-3})	$< 5 \times 10^{14}$
Cutoff Wavelength at 77K (microns)	10.0 - 10.5
Cutoff Wavelength Uniformity at 77K (microns)	± 0.3
Hall Mobility at 77K (cm^2/V-S)	$> 1.0 \times 10^5$
Hall Mobility at 20K (cm^2/V-S)	$> 1.0 \times 10^5$
Minority Carrier Lifetime at 77K (usec)	> 1.0
Etch Pit Count (cm^{-2})	$< 1.0 \times 10^5$
Length (inches)	> 1.00
Width (inches)	> 0.50
Density of Voids, Inclusions, Etc.	None > 6 microns in center 0.80" x 0.30". , <10, >15 microns elsewhere

This technique will be useful in the short term but is too cumbersome to scale up to produce the material quantities needed in the 1992 time frame.

The growth technique that has the potential for meeting the quality and quantity requirements is the traveling heater method (THM) of HgCdTe crystal growth. The THM process has produced extremely high quality material but on a very limited basis. Because of the present lack of process control, yield numbers are not meaningful points of discussion. There are three major problems facing THM crystal growth. They are:

- Compositional variations from ingot to ingot and within an ingot give rise to deviations from the desired 10 micron cutoff wavelength.
- Microstructure such as dislocations, sub grains, and voids limit device performance and producibility.
- Polycrystalline growth limits the quantity of single crystal material contained in the ingot.

Once these problems are overcome the THM process can be inserted into a manufacturing environment.

Program Overview

An intelligent processing program is proposed for the controlled growth of HgCdTe by the THM technique. The program proposed will consider the entire THM growth process; source material production, actual THM growth, and heat treatment of the grown ingot. It will contain the following major thrusts:

- Modelling to define the critical parameters in the growth process and to provide guidance for improved technique. Key material constants will be measured. Outside consultants that are expert in this field will be utilized to help guide this effort.
- Experimentation to validate models and evaluate new concepts. Two THM growth facilities exist with a combined total of 22 furnaces. This capability offers the opportunity to run several parallel experiments and build a significant data base.
- Sensor development continued for monitoring critical process parameters. Eddy current techniques will be evaluated for measuring interface shape and melt volume. Fiber optic thermometers will be tested for precision temperature measurement. A mercury pressure manometer will be implemented to monitor the mercury partial pressure during growth. Other techniques such as nuclear gauging UV reflectance, X-ray, ultrasonics, and methods dictated by modelling results will also be examined. The initial stages of closed loop control will be completed.
- Characterization of the grown material in terms of electrical and physical properties conducted throughout the program.
- Intelligent processing techniques and methodology relevant to the THM process developed. TI has developed a strong technology base in expert systems and artificial intelligence. This will be exploited early in the program to begin structuring the interrelationship of the various sensors to the growth model and ultimate manufacturing process control.

HgCdTe Technology at Texas Instruments

Background

The first FLIR, invented at TI in 1964, used photoconductive detectors made of mercury-doped germanium. The low quantum efficiency and inflexible cutoff wavelength of this material were soon recognized as serious limiters in the design and fabrication of IR detector arrays for many applications. HgCdTe, because of its inherently high quantum efficiency and composition-tailorable bandgap, offered a potential solution to these problems. A Research and Development (R&D) program was thus initiated at TI in the mid-1960's to develop this new material.

Early attempts to grow single crystals of HgCdTe were made using the solid state recrystallization (SSR) method which involves, (1) melting HgCdTe in a small fused-quartz ampoule (eg. 12mm x 125mm), (2) anisotropic quenching with a gas jet, (3) recrystallizing the highly defected dendritic structure at a temperature just beneath the solidus, (4) sawing wafers from the ingot, and (5) postannealing at a low temperature under Hg vapor to convert the material from $\sim 10^{17}/cm^3$ p-type to $<10^{15}/cm^3$ n-type. A production SSR process was successfully developed in the late 1960's and is still used today as the main source of HgCdTe for IR detector manufacture at TI.

SSR HgCdTe has adequately low carrier concentration and uniform cutoff wavelength for IR detectors. However, it also has low crystalline perfection; i.e., less than half the material recrystallizes and that which does recrystallize contains small, randomly oriented single crystals with typically $>10^5/cm^3$ random dislocations and a high density of subgrain boundaries. These defects do not seriously affect the performance of photoconductive detector arrays, but they do enhance tunneling dark current in MIS detectors and thereby degrade the performance of FPA's. Consequently, SSR HgCdTe slated for FPA manufacture must be carefully screened for microstructure, and the yield of acceptable material is always below 10 percent.

In the late 1970's, programs were initiated at TI to develop processes for growing large-area, low-defect-density HgCdTe for FPA's by both liquid phase epitaxy (LPE) and metal organic chemical vapor deposition (MOCVD). A horizontal Bridgman CdTe process was concurrently developed to provide the required single crystal substrates. Today, high-performance Medium Wavelength Infrared (MWIR) FPA's are routinely produced from LPE HgCdTe grown in the laboratory, and a program to establish this technology in production by 1990 is underway. Long Wavelength Infrared (LWIR) LPE is less advanced, however. R&D continues in an attempt to eliminate the doping inhomogeneities in this material that are responsible for poor Metal Insulator Semiconductor (MIS) detector performance. The Metal Organic Chemical Vapor Deposition (MOCVD) HgCdTe process is even less advanced. Primarily because of high impurity concentration, quality MIS detectors have not been demonstrated on MOCVD material at any cutoff wavelength.

In 1984, TI began research on HgCdTe growth by molecular beam epitaxy (MBE). In this case, the intent was not to develop a growth method to supercede SSR, but rather to provide specialty bandgap-engineered materials in support of advanced device physics R&D aimed at development of multicolor detectors, detectors with very long cutoff wavelengths (>20 microns), and II-VI integrated circuits. This work is progressing well in the laboratory. Both HgTe/CdTe superlattices and CdTe/HgCdTe heterojunctions have been grown and MIS devices have been successfully fabricated on them.

Traveling Heater Method (THM)

By the early 1980's it had become evident that none of the available HgCdTe growth methods could generate HgCdTe suitable for high-volume manufacture of LWIR MIS FPA's. High-performance MIS detectors could not be made on LWIR HgCdTe grown by either of the thin film techniques, LPE and MOCVD. Detectors with good average performance could be made on bulk SSR material, but its random crystal orientation was not compatible with reproducible FPA batch fabrication and its high density of crystalline defects led to low material yields and non-uniform pixel-to-pixel performance across FPA's. A new approach to HgCdTe growth was needed, one that would yield large, oriented, high-purity single crystals with a low concentration of crystalline defects. The THM method offers the potential for growing HgCdTe with these characteristics.

The THM concept is shown in Figure 1. This concept is simply a variant of LPE wherein the period of epilayer growth is extended from minutes to days in order to form a large single crystal ingot. As in LPE, a high melting point HgCdTe crystal is expitaxially nucleated on a CdTe seed from a slightly supercooled low melting point Te-rich solvent.

As growth proceeds by lowering the ampoule down through a thermal profile imposed by external heating elements, the melt is continuously replenished by dissolution of a HgCdTe source of the same composition as the grown crystals.

TI's early approach on THM was heavily weighted towards gaining practical experience with the new methods and hardware. The experimental philosophy was to establish a set of growth conditions, grow an ingot under those conditions, perform metallurgical and electrical evaluations, and use the results to formulate a new set of growth conditions designed to yield a better ingot on the next growth run. A large database of practical cause-and-effect information has resulted along with two facilities containing a total of 22 reactors. In addition, and of utmost importance, MIS test detectors made on LWIR THM HgCdTe from some of these ingots have demonstrated the highest performance ever recorded.

THM Growth Facilities

Facilities are in place at TI for the THM growth of HgCdTe. These areas provide for both the statistical design of experiments and testing and implementation of sensor and control technology. The S/C Pilot Line facilities contain ten thermally equivalent furnaces with complete rotation and translation capabilities in which a statistical experimentation matrix such as that provided by the Taguchi or ECHIP method can be utilized. The TI North Building Process Development facilities provide six additional furnaces which are currently being modified for rotation and translation. These furnaces will then be thermally equivalent and can be used for additional statistical matrix experiments. The remaining six furnaces in the TI North Building are used for Engineering R&D purposes.

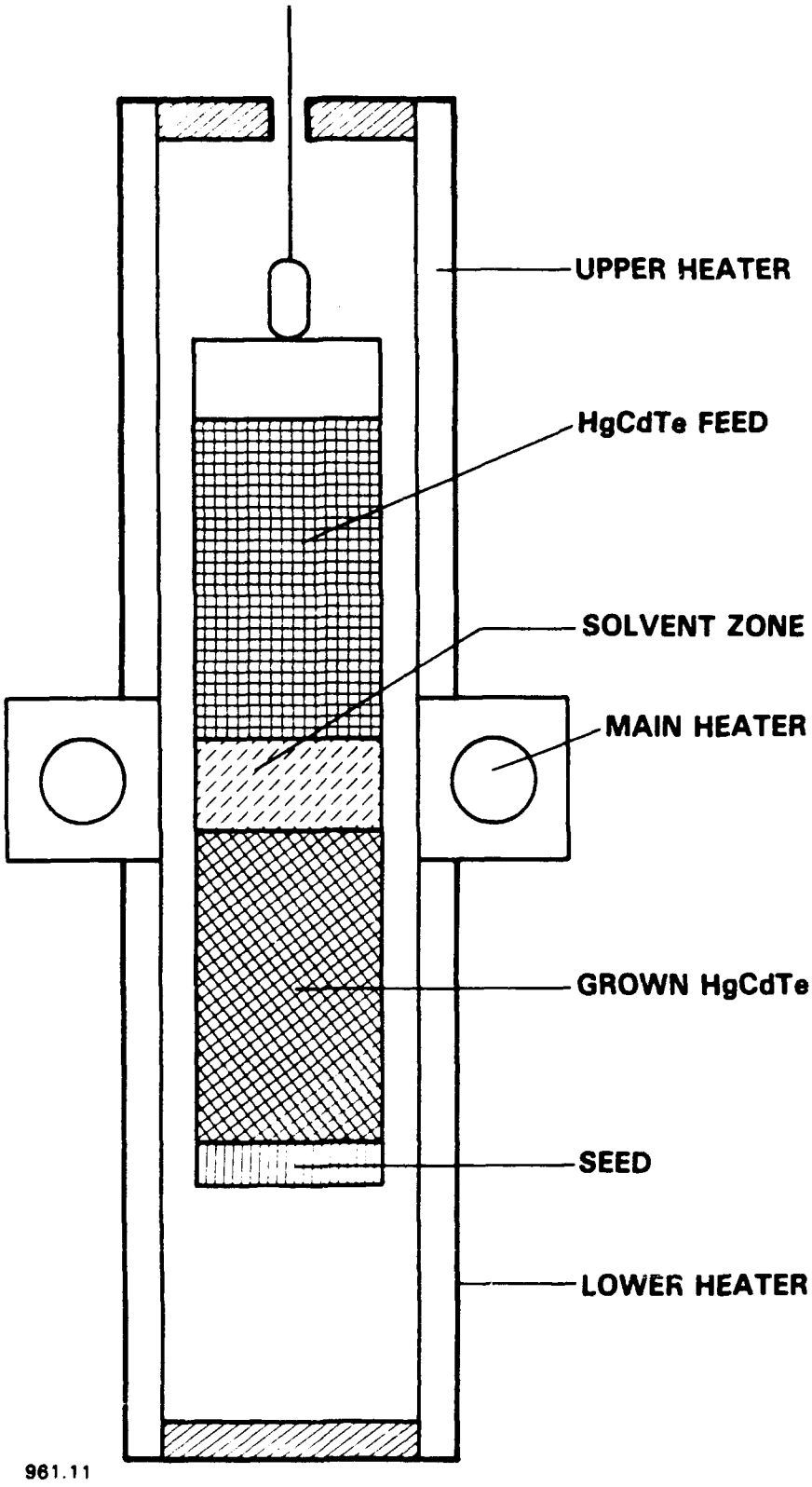


Figure 1. THM Growth Configuration

Program Plan

Modelling and Parametric Measurements

Process Modelling Considerations. The objective of developing models for the various processes in the growth of HgCdTe by THM is to determine the relative importance of the process parameters, to establish their ranges and to provide the basis for developing automation and process control. A most general model of the THM growth process incorporates closely coupled effects of heat flow in the THM ampoule and furnace environment as well as fluid flows and mass transfer and the phase equilibria tieline relations in the solvent area. The model must also describe the strain fields generated by temperature and composition gradients in the growing crystal and by the presence of ampoule walls. Such a comprehensive model, as described schematically in Figure 2 is difficult to formulate and computationally intractable. As experience is gained with the growth process, the formulation of a model that incorporates all the salient features of the process will be pursued. Commercially available software for solving coupled time dependent non-linear differential equations (such as MATHEMATICA, FLUENT/NEKTON/FIDAP, LQG CONTROL, MSC/MAGNETIC) will be evaluated as it becomes necessary.

TI has begun modelling by decoupling the thermal management of the growth system (heat transfer) from the mass transfer of Hg and Cd in the solvent. Heat transfer analysis as shown in Figure 3 provides the basis for estimating temperature profiles and temperature gradients in the solvent and solid crystal and source material in general and most importantly in the solid-liquid interfaces. The temperature gradient in the solvent at the growing interface determines the growth rate range and the composition as shown in Figure 4. Growth rate considerations are incorporated in the companion thermodynamic and mass transport model.

Thermal Modelling. A finite element quasi-steady-state thermal model to simulate the growth of HgCdTe by the traveling heater method was developed.[1] Newton's iteration scheme is used to efficiently solve the free boundary problem associated with the search for the solvent/crystal interface locations, together with the implementation of Hood's frontal method to minimize the memory required for matrix manipulation. The ampoule region is incorporated into the thermal model and forms the basis for comparing the simulation results with experimental measurements. Sensitivity studies were carried out to explore the change of interface shape due to variations in thermophysical parameters, physical dimensions of the system, thermal boundary profile, and crystal growth conditions. The interface shape was always concave at the solvent/crystal/quartz-wall three-phase contact point regardless of whether the macroscopic interface shape was concave or convex. This local concavity was due to the higher quartz-wall thermal conductivity with respect to that of the growing crystal. The modelling interface shapes were in good agreement with experimental observations, except that a major deviation exists at the three-phase contact point where the model predicts a higher concavity than that observed experimentally. This discrepancy may be due to convection flows in the solvent. With the aid of the model simulation, slightly convex macroscopic interface shapes can be achieved and maintained for the single crystal growth of HgCdTe. A consequence of our thermal management modelling was the introduction of the infinite stem growth process. The infinite stem technique uses a charge of HgCdTe under the oriented seed in order to immediately establish a steady state thermal environment. As predicted from thermal modelling, the infinite stem mimics the heat flows that exist well into the growth cycle, eliminating early growth transients and uncontrollability. This is essential to composi-

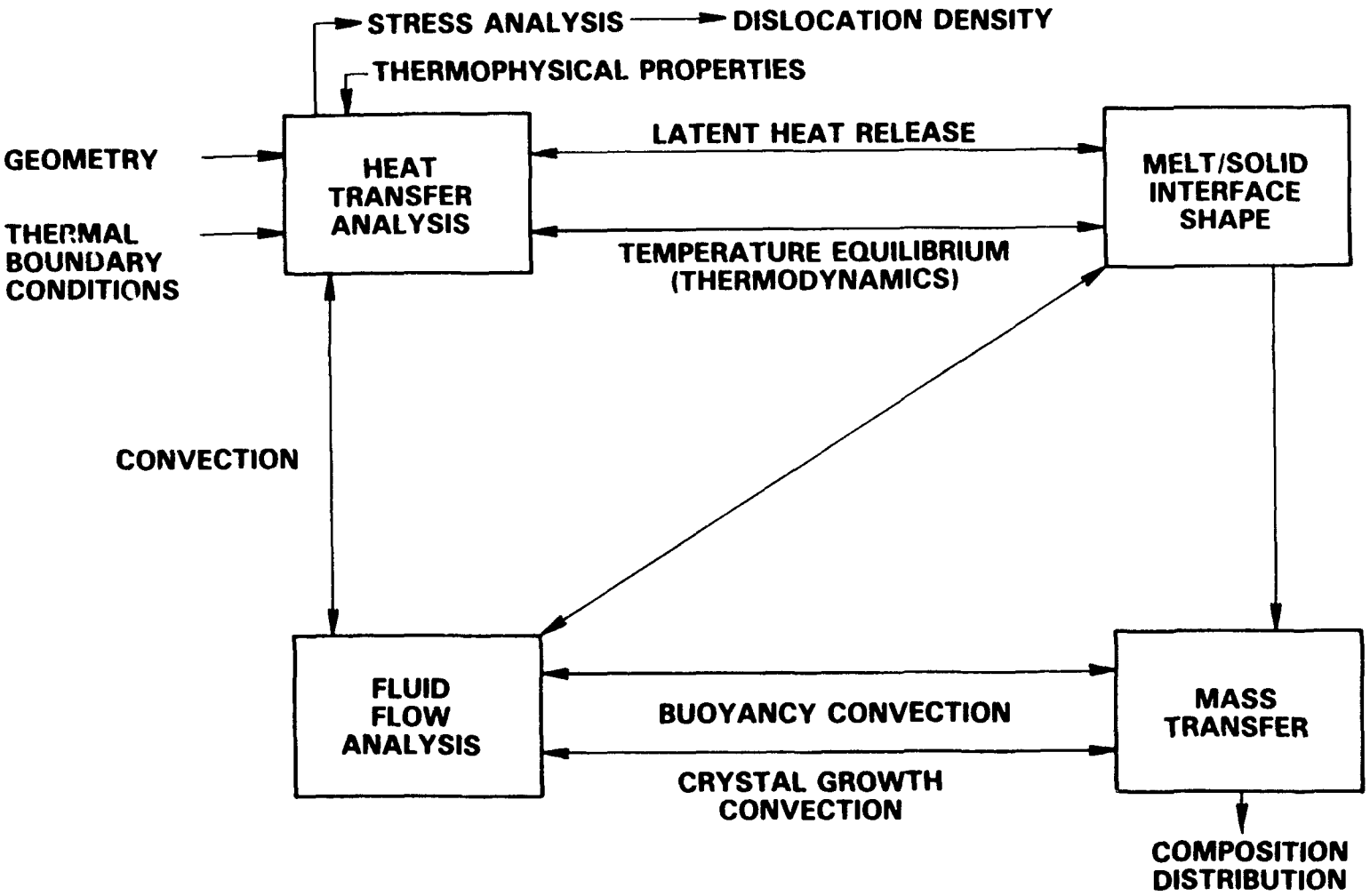
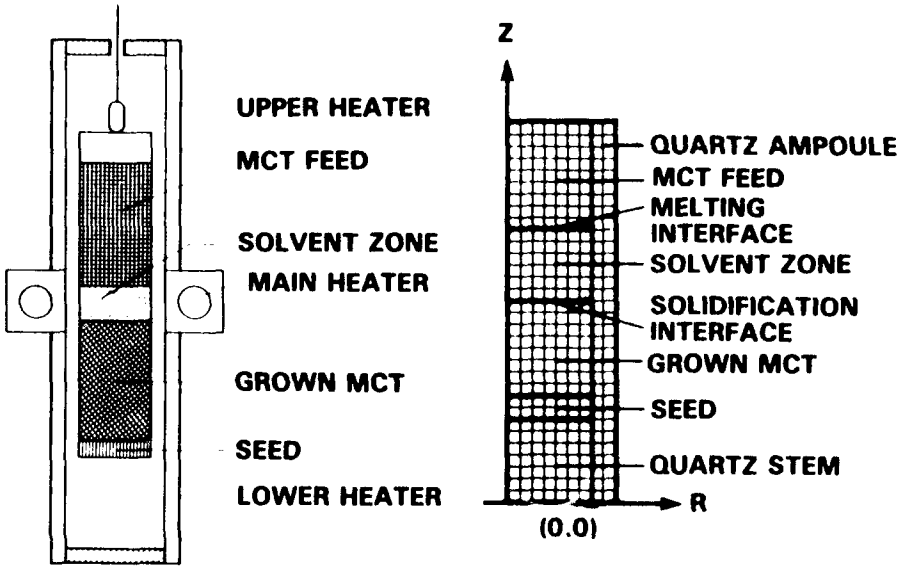
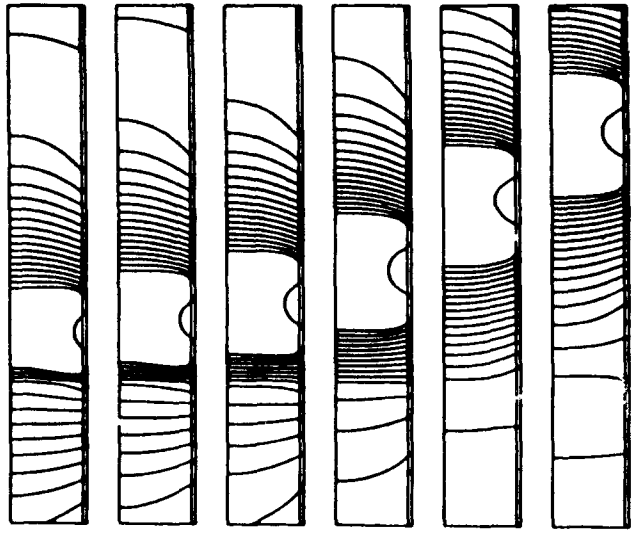


Figure 2. Mathematical Modeling of Crystal Growth from the Melt

- FINITE ELEMENT THERMAL MODEL
- RUNS ON A PERSONAL COMPUTER
- PREDICTS INTERFACE SHAPES
- AGREES WITH EXPERIMENTS





- INTERFACE SHAPE CRITICAL TO SUBSTRUCTURE AND UNIFORMITY
- MODEL ALLOWS OPTIMIZATION OF INTERFACE SHAPE DURING GROWTH

961.2

Figure 3. Thermal Conduction Model

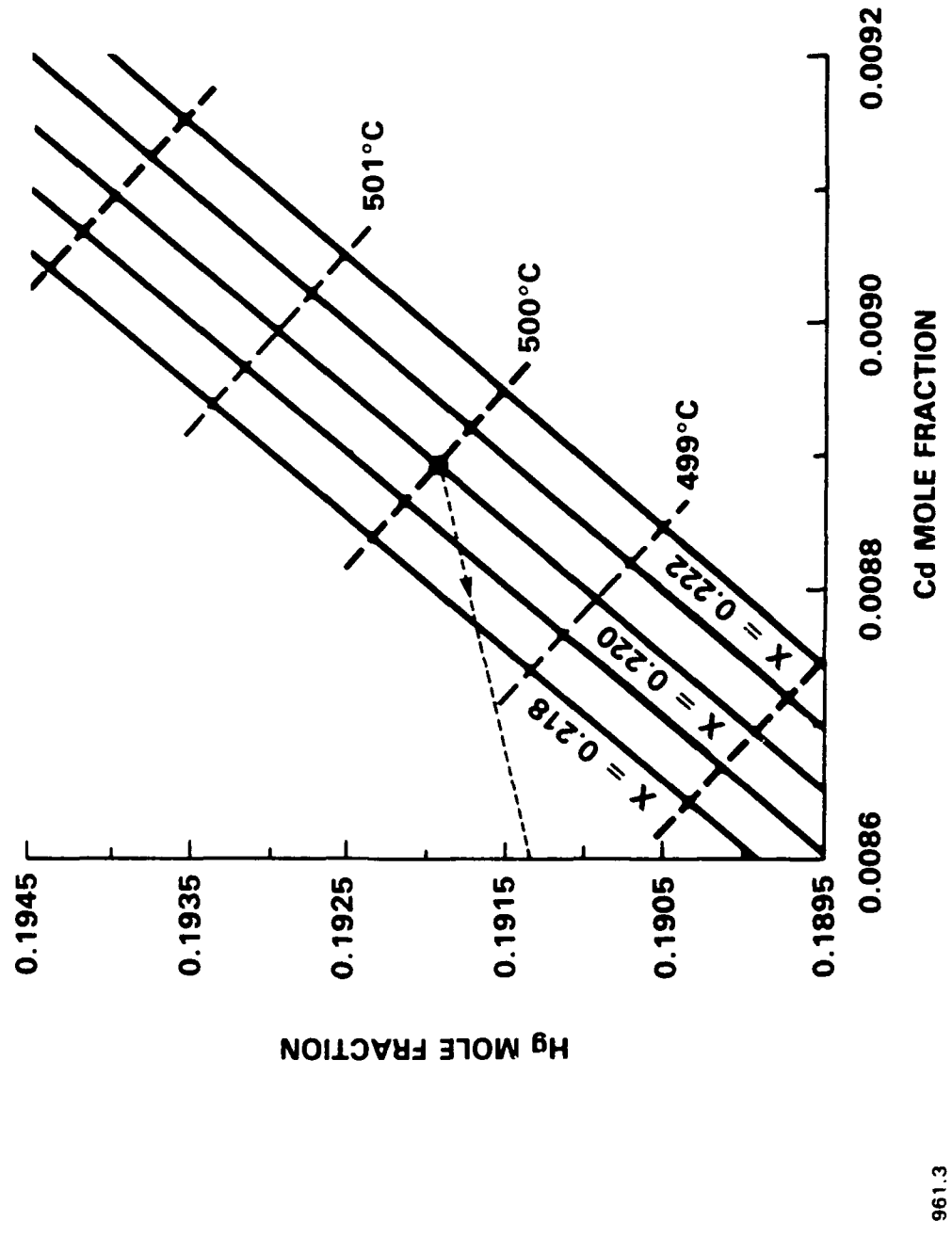


Figure 4. Thermodynamic Model

tion control and material yields in a pilot line environment because of the slow growth rates used in THM. The HgCdTe stem was successful in establishing and maintaining the convex interface essential to single crystal growth.

Thermodynamics and Mass Transport Control Modelling. The thermodynamics and phase equilibria which govern the growth of the crystal from the melt have also been modelled. Assuming that thermal management of the growth system has been achieved and that temperature profiles are described by the above heat transfer model and that the process is in a diffusion controlled environment, the growth of HgCdTe by THM was modelled one-dimensionally along the growth direction. Alloy composition of the as-grown solid as a function of time was calculated from the temperature and the solvent composition adjacent to the growing interface. A numerical simulation of the growth of HgCdTe by liquid phase epitaxy developed by Shaw was modified to match the THM configuration.[2] The model coupled the mass transfer of the constituents Hg and Cd in the Te-rich melt by finite difference methods and the phase equilibrium tie-line relations by the associated solution model for the liquid phase.[3] The equilibrium partial pressure of Hg generated at the growing interface was also introduced in the calculations so that it might be further investigated and eventually used in the control of the melt composition through a Hg reservoir in a separated, controlled temperature zone. Table 2 shows the equilibrium temperatures for the growth interface and the mercury reservoir.

Process Simulation. As described in the thermal and thermodynamic models, temperature profiles and growth rate evolution during THM growth appear to be the main parameters for an expert system control of the process. Therefore, a first order analysis will be based on the modified Shaw model, mentioned earlier, to be completed during the early part of the pro-

TABLE 2. Hg PRESSURE CONTROL

Hg partial pressure over Te-saturated melt in equilibrium with $Hg_{0.78}Cd_{0.22}Te$ solid solution for $480 \le T_G \le 520^{\circ}C$

$$\text{LOG } P_{Hg}(\text{atm}) = -6340.18 / T_G + 7.3104 \qquad (1)$$

where T_G is the growth temperature in K

Hg vapor pressure over pure liquid Hg

$$\text{LOG } P_{Hg}^{0}(\text{atm}) = -3099 / T_R + 4.920 \qquad (2)$$

where T_R is the Hg reservoir temperature in K

by equating (1) and (2)

$$T_R = -3099\ T_G / (-6340.18 + 2.3904\ T_G)$$

T_G	480°C (753.15 K)	500°C (773.15 K)	520°C (793.15 K)
T_R	240.97°C (514.12 K)	260.24°C (533.39 K)	279.92°C (553.07 K)

gram. The thermal model will provide simulated temperature profiles. Actual temperature profiles will be provided by the eddy current probe profiler after its development. The thermodynamic model will predict the growth rate (ampoule travel rate) as a function of growth time. The validity of this modelling will be verified by growing crystals with different diameter where the thermal conditions will be different.

The THM growth of HgCdTe will be also simulated with near room temperature THM growth process of solute-solvent systems such as naphthalene (solute)-benzoic acid (solvent) and other such systems to be identified.

Measurement of Material Constants. The development of process models and simulation requires accurate data on those material properties that enter into the model calculations. Such properties are the electrical conductivities of the Te solvent, of the HgCdTe growing crystal and of the source material, and their temperature dependence. Electrical conductivity data are required to develop imaging of the interface shape in real time using eddy current profiling. For this reason electrical conductivity and Hall coefficient of the solvent and of HgCdTe source and single crystal material will be measured as a function of temperature for the THM growth temperature range. The eddy current profiling probe provides another means of measuring the electrical conductivity of the material inside the growth ampoule. Such measurements will in fact provide direct measurements of the mercury vacancy concentrations in the 200°C to 550°C temperature range, where various heat treaments of the material are performed.

Other properties that enter the process thermal and mass transport models include the thermal conductivities of the quartz ampoule, of the CdTe seed and of the liquid HgCdTe alloy, and their optical absorption coefficients in the near infrared. These properties affect the temperature profile that can be established in the THM system. The establishment and properties mass transport boundary layers in the solvent is dependent on the Prandl number and other mass transport dimensionless coefficients of the solvent. The temperature dependence of the density of the solvent plays a role in the convection current configuration. The literature values of these parameters will be used if available. If unknown, sensitivity analysis of the process models will establish their relative significance and the degree of needed accuracy that they have to be measured for adequate process control. Appropriate measurements of such material parameters will be undertaken at TI or will be subcontracted to academic institutions.

Growth Experiments and Model Validation

Compositional Uniformity. A series of experiments addressing compositional uniformity will be performed off line. These include studies of the Incremental Quench (IQ) Compounding Process, induction heating of the solvent, and direct measurement of the mercury pressure in the THM ampoule. These experiments are detailed in the following paragraphs.

The materials characteristic with the most uncontrolled variation is the composition of the THM crystals. The IQ compounding process is a significant source of that variation. Density stratification of the melt prior to quenching is the most likely source of variation as shown in Figure 5. Mixing of the compounded melt within the high pressure vessel will be carried out to the extent needed to establish a homogeneous IQ ingot. The THM process will not achieve the desired compositional uniformity if the IQ is not similarly uniform on a macroscopic

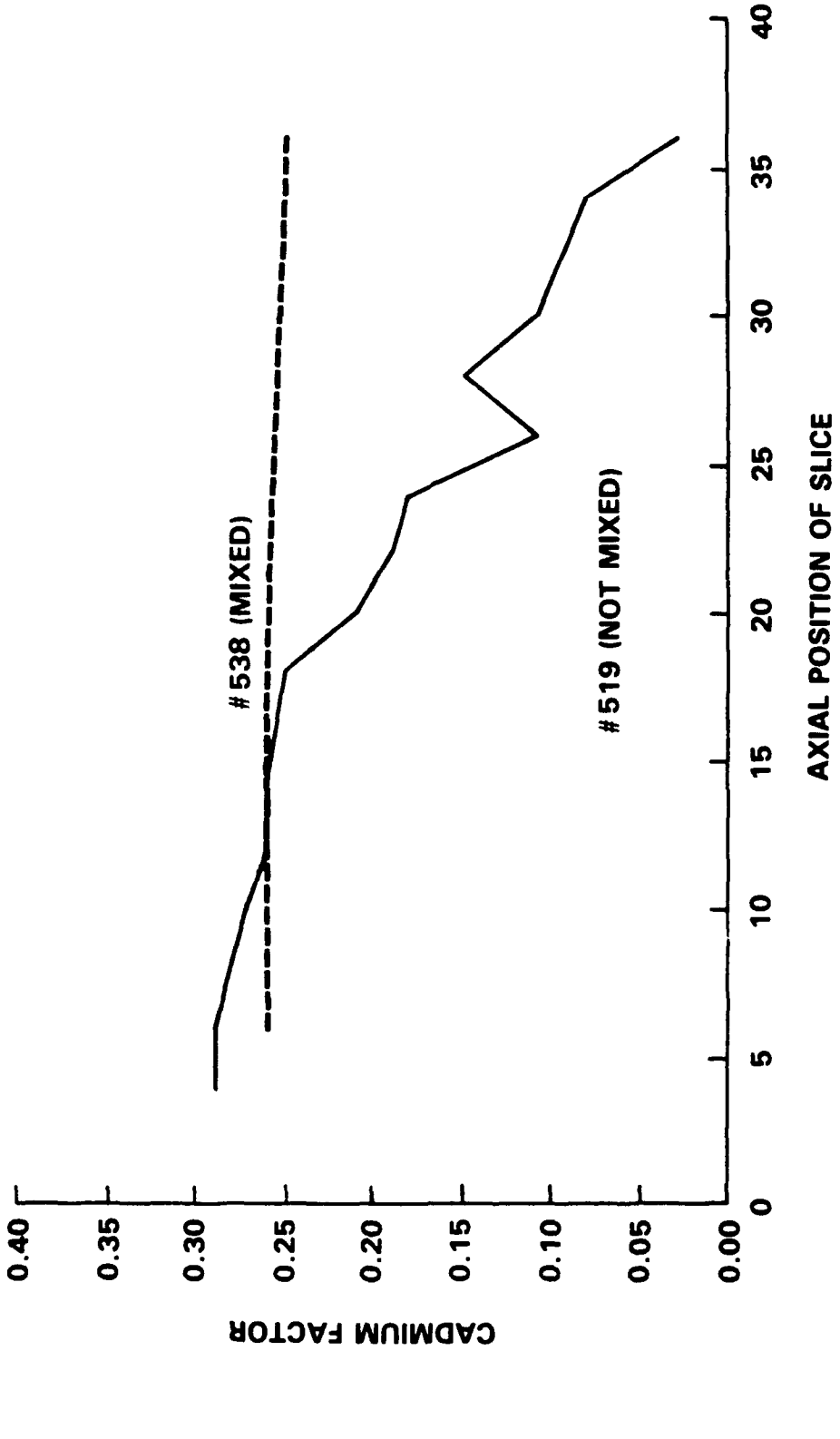


Figure 5. Incremental Quench Ingots

scale. At present the IQ compositional uniformity is controlled by thermal management during the quench procedure. This has not been totally successful. During this program, a sensor will be used to optimize and control the preparation of the IQ source ingot. Variation of the IQ compositional uniformity is a limiting boundary condition on the performance of the traveling heater method for the growth of large single crystals of HgCdTe. A uniform IQ is a necessary but not sufficient condition for a uniform composition THM crystal growth process. HgCdTe is an incongruent melting solid solution, i.e., the compositon of the solid crystal growing from a tellurium rich melt is very different than the composition of that liquid. Several stability problems have been identified and potential solutions have been invoked on our experimental growth equipment. Two methods of THM growth have been used. In the first method, a mercury reservoir was established in a cup on top of the source ampoule as shown on the left ampoule in Figure 6. This arrangement does not permit condensation of mercury back into the cup, since by definition of the thermal gradients, the coldest surface in the ampoule is the wall of the ampoule near the convection cooled top end. Evaporation of mercury in the cup is condensed on the wall where it is gravitationally fed to the solvent zone below as the condensing droplets grow beyond a stable size. This size is determined by the wetting of the mercury to the quartz tube surface. A second problem is that the hydrostatic head caused by the weight of the source ingot squirts solvent down past the seed and up around the source until the solvent reaches the colder zones and temporarily freezes the source in a fixed position. Thus it can not decend any further into the solvent. A discontinuous walk of the source ingot occurs during continued growth as the solvent zone passes through the lost and previously frozen solvent. This configuation is not stable and, therefore, very difficult to control by any new sensor technology.

The other established growth method, has been more successful. It is based on filling the void between the source, solvent, seed and stem with molten tellurium as the stack is placed in a single zone furnace at about 500^{o}. This "capped" melt does limit the mercury loss from the solvent zone in the absence of a reservoir due to the limited diffusion of mercury in the gap between the tellurium cap and the wall of the quartz ampoule. It also freezes the source ampoule in position where it probably does not move uncontrollably during melting of the solvent or later in the growth. However, the additional tellurium that is dissolved in the solvent during growth changes the solvent composition. The dilution effects of additional tellurium have been avoided by the use of a solvent composition instead of the pure tellurium for the capping of the stack of components in the THM ampoule. The process presently being used in the pilot line is a "solvent cap" process which still suffers from the increased size of the solvent zone due to the peripheral solvent cap being incorporated into the solvent during growth. This increased solvent zone volume forces a change in the temperature gradient on the crystal growth interface and forces a change in the composition of the growing crystal. The solvent zone volume and composition is a major source of variation in the THM crystal growth process.

As part of this proposed program, the "NEW" ampoule design shown on the right side of Figure 6 will be evaluated. Several ideas have been incorporated into this design that should help to improve the dimensional and theromodynamic stability of the THM process so that a steady state growth process can be achieved and controlled. Equilibrium with the mercury vapor pressure is a desirable goal and should be controlled by a mercury reservoir that is located at the coldest region of the ampoule; the wall. A constriction of the closure of the ampoule is shown with appropriate vented openings to permit condensation on the wall. The constriction should permit a small amount of excess mercury to collect on the wall and limit

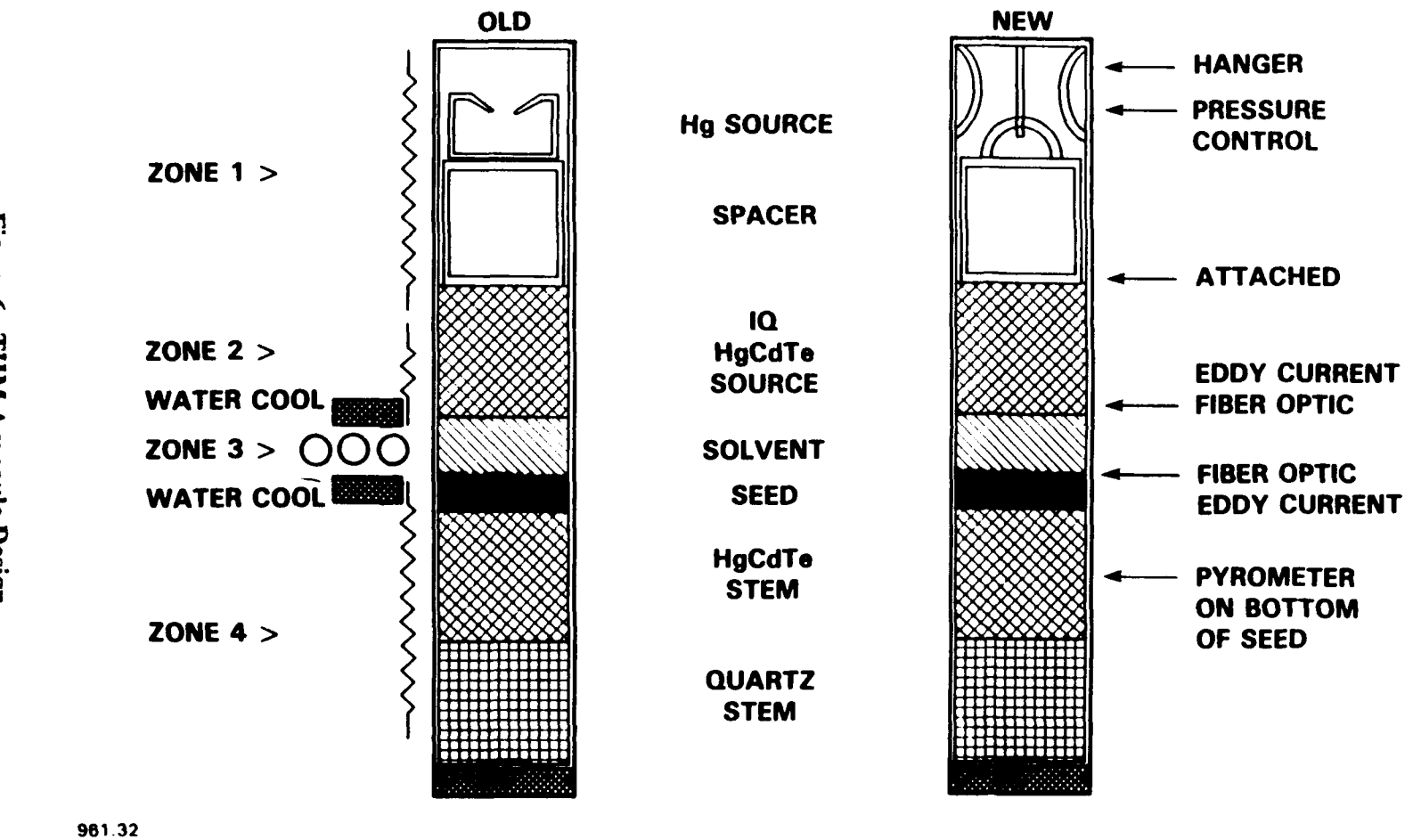


Figure 6. THM Ampoule Design

its gravitational decent to the region of the constriction. There is no requirement for this mercury reservoir if there is not sufficient plennum for the gas phase to equilibrate with the solvent. A hanger is also shown which supports the source ingot above the solvent removing the hydrostatic pressure of the weight of the source on the melting solvent. This hanger should secure the solvent in the molten zone and limit the solvent loss that has always been observed with uncapped ampoules.

The temperature of the mercury reservoir will be used to control the flux of mercury between the solvent and the reservoir. The partial pressure of mercury over its pure condensed liquid at about 270^{o} is equivalent to the partial pressure of mercury over the solvent at the much higher growth temperature of 460^{o}. Since the temperature of the solvent is fixed by the thermal and mass balance at the source ingot and crystal growth interfaces, the mercury flux to or from the solvent zone can be controlled by changing the temperature of the mercury reservoir. Since the evacuated ampoule achieves a mercury pressure of about one fourth of an atmosphere during growth, the composite pressure is a measureable and controllable variable; i.e., the temperature of the mercury reservoir will be changed to hold the mercury pressure constant during the run. In the present situation the Hg pressure is changing due to the change in reservoir temperature as the ampoule moves within the furnace. The solvent equilibrates with that change in pressure by loosing or gaining mercury. The compositon of the solvent and its volume are therefore observed to be a strong function of not only the temperature at the source and crystal interfaces but also the temperature gradient on the THM ampoule. The mercury pressure in the ampoule during growth will be measured and controlled to establish a uniform composition of the MCT crystal at the desired value of the mercury to cadmium ratio.

The absolute temperature of the crystal growth interface will be measured using a precision fiber optic thermometer as shown in Figure 6. The eddy current analysis of the solvent zone will also be a very important and sensitive measure of not only the solvent volume but the actual shape of the crystal growth interface. It is important to realize that the ultimate validation of the model is the reproducible control of the composition of the crystal as measured after growth.

Microstructure. Both X-ray topography and defect etching of recent HgCdTe single crystals produced by the THM process reveal the basic subgrain structure that is characteristic of all THM and SSR materials to date. Potential causes of this substructure are substructure or dislocations in the seed; lattice mismatch between the seed and the initial growth composition; stresses created by the local variation in composition of the grown crystal; stresses created by the high temperature gradients; stresses created by the constraints of the ampoule wall; stresses created by the incorporation of second phase; and stresses created by the freezing solvent as the growth process is shutdown.

As part of this program improved quality seeds will be used to reduce the microstructure caused by the present CdTe seeds. Cadmium zinc telluride (CZT) seeds with a better lattice match will be used. THM grown seeds of HgCdTe and CdZnTe will be used to grow reduced microstructure crystals. Commercially available, CdZnTe seeds have demonstrated better dislocation density than the internal supply.

Improved control of the seed melt back and the initial growth interface shape will impact the quality of the first HgCdTe to freeze on the seed.The impact of reduced melt back is to limit the lattice mismatch stresses created by large deviations in crystal composition. A convex interface shape propagates dislocations toward the crystal surfaces during the growth process. Considerable stress has been observed in the process by the imposed high gradients that define the growth interface and discourage constitutional supercooled second phase as well as entrapped solvent. Fracture is the ultimate limit on these gradients now but there may be some major improvements in microstructure possible with reduced thermal gradients.

Experimental Design. Conventional engineering methods for tuning up the process and assigning causal relationships will also be carried out on this project on the more mature and controlled experiments.

In a process such as THM, which is affected by multiple control variables and involves long experimental lead times, it is essential to maximize the knowledge to be gained by changing the control parameters in a most expeditious manner. This can be accomplished through a statistical design of experiments in which many variables are studied simultaneously.

One such method of statistical design is known as ECHIP. This method is similar to the better-known Taguchi method which seeks to render design of manufacturing processes insensitive to environmental and uncontrolled variables. In both methods relevant variables are chosen and their ranges varied simultaneously according to a statistical design matrix. The system response to these variations is then observed and analyzed. ECHIP has an advantage over the Taguchi method in that an option is provided to decide on the required resolution (the smallest change in a response variable deemed of practical importance). Screening is used to eliminate unimportant variables, especially those that create noisy data not within the process region of interest. This option significantly reduces the number of experiments necessary to obtain the same amount of information. The total cycle is thus: 1) decide on the required resolution; 2) choose the control variables and their ranges; 3) design the experimental matrix; 4) run the experiments; 5) enter and analyze the data through contour plots; and 6) report the results.

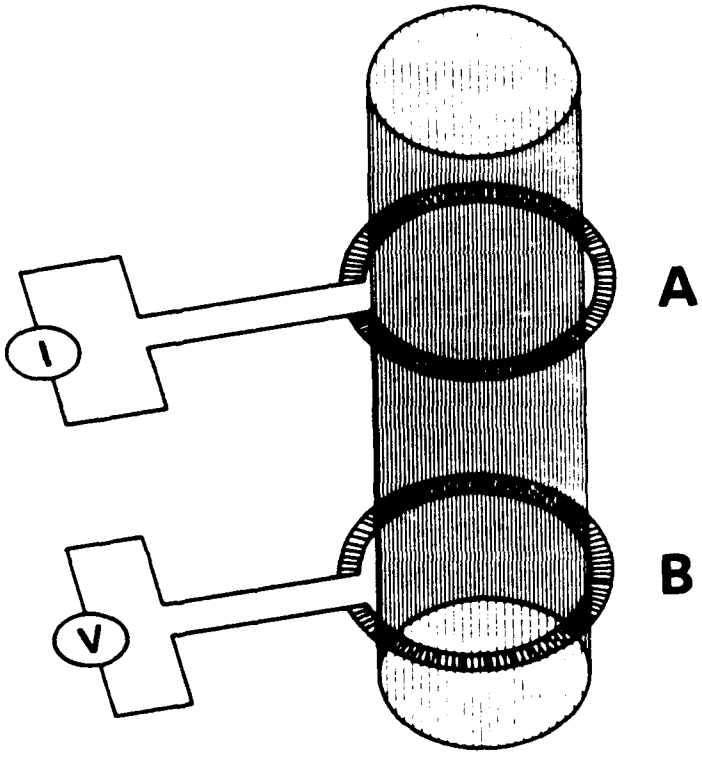
An essential criteria which must be met in order for the experimental design to be valid is adequate control over the input variables. The input variables in the case of the THM process include such items as temperature at the interface, volume of the solvent zone, thermal gradient, growth rate, mercury partial pressure, and rotation rate. The response variables might include microstructure, radial and axial uniformity, and electrical properties. At the present, techniques are being implemented within the growth process which allow monitor and, more importantly, control of the input variables. Implementation of these techniques will allow an experimental design method such as ECHIP to be utilized to further optimize the growth process. Currently, ECHIP is being used to develop experimental design matrices for several after-growth processes such as annealing and surface planarization which also affect the response variables.

Sensor Development and Implementation

Eddy Current Analysis. Eddy Current Analysis (ECA) has been used for many decades in all of the metal working and fabrication industries to assess the surface and internal structures of metal parts.[4] It is insitu and completely noninvasive. Surface defects, voids in castings,

and solidification rates of metals inside molds are typically determined.[5] The method measures the amplitude and phase of reflected low frequency RF radiation as a function of frequency. Then, with appropriate real-time computer analysis of the data, detailed information can be derived about a given process. For example, this technique can detect a scratch 0.002-inches deep on the surface of a 0.4-inch OD steel rod.

ECA works by inducing a time varying current in a conductive part and then measuring the electromagnetic waves emanating from those induced currents. Consider the encircling coil arrangement shown in Figure 7. Here a cylinder of conductive material is encircled by coils A and B. If a time varying current is imposed in coil A, then currents of the same frequency will be induced in the conductor. Electromagnetic flux from these currents will, in turn, induce a voltage in coil B. The voltage induced in B will depend on the frequency of the excitation current and on the exact internal structure of the conducting part. The lower the frequency, the deeper the induced currents will penetrate into the rod. By measuring the B voltage at a number of different frequencies at one axial position, a nearly exact picture of the radial structure of the rod is obtained.[6] If the coils are moved along the rod axis, the axial structure can be determined as well. ECA measures electical conductivity variations. Thus, any material property that can be correlated with a conductivity change can be measured by ECA. These properties would include, for example, the positions of interfaces across which there are significant conductivity changes. Also, if the conductivity of a liquid metal system is dependent on composition, then the composition can be measured directly by ECA. In semiconductor crystals, the conductivity (in the intrinsic range) is temperature dependent. Thus, the temperature profile in a crystal being grown by the Czochralski process can be measured insitu.[7] It is these types of measurements that can benefit THM growth of HgCdTe.



961.16

Figure 7. Encircling Coil Arrangement for Eddy Current Analysis of THM Growth

Application of ECA to THM Growth of HgCdTe. Flaw testing only requires the detection of a signal change compared to a baseline. Thus, a flaw detection system can be highly non-linear and still work very well. To actually measure properties, however, requires a very linear system. To achieve the goals of the investigation the same equipment will be used that has been successfully applied to the insitu analyis of silicon crystal growth.

The main problem in the current THM approach is variation in the solid composition. This is thought to be caused primarily by variations in the liquid zone composition. Assumming a constant composition source, this variation is apparently caused by variations in the liquid volume. To control this process it is of primary importance to control both the volume of the liquid zone and the shapes of the two interfaces that bound the liquid. To control these, they must first be measured.

The current THM furnace configuration lends itself ideally to ECA analysis by encircling coils. This is because encirlcing coils can be built into the chill blocks that bound the central heater (and thus, the liquid zone) without modifing their thermal function. To measure the extent of the liquid zone, including interface shapes, a vertical stack of coils can be built into each chill plate (see Figure 8). The coils can then be multiplexed absolutely or as differential pairs. Plans currently exist to build eight coils into each block. Each coil will be run at four different frequencies simultaneously. The data will then either be inverted directly or matched to a forward model to determine the state of the system.[8]

Preliminary experiments were conducted with available sensors. Figure 9 shows the signal change in phase and amplitude as HgCdTe solidifies. Figure 10 demonstrates the signal magnitude as a THM ampoule is moved past the sense coils. From this data an estimate of the ratio of the electrical conductivity of the liquid to solid in the THM system has been found to be on the order of 20 to 1. The liquid is much more conductive than the solid. This will allow for a very accurate determination of interface shape and position.

Aside from applying ECA to full THM runs, four sets of basic investigations are immediately evident. These include:

1. Measurement of the conductivity of solid HgCdTe over the range 20°to 700°C. This will probably require frequencies up to 5.0 MHz. This will allow the measurement of temperature gradients in the solid and, consequently, thermal stress.
2. Measurement of the conductivity of the solvent as a function of composition and temperature. If there is a measureable change of conductivity with composition, this will allow a direct determination of solvent composition by ECA.
3. Measurement of the complete cooling curve by solidification of the solvent. This involves the rapid cooling of the normal THM configuration. It will allow the determination of the two phase properties of the system.
4. Measurement of the complete four frequency eddy current profile of the system. This involves rapidly moving a normal THM ampoule through the eddy current sensors.

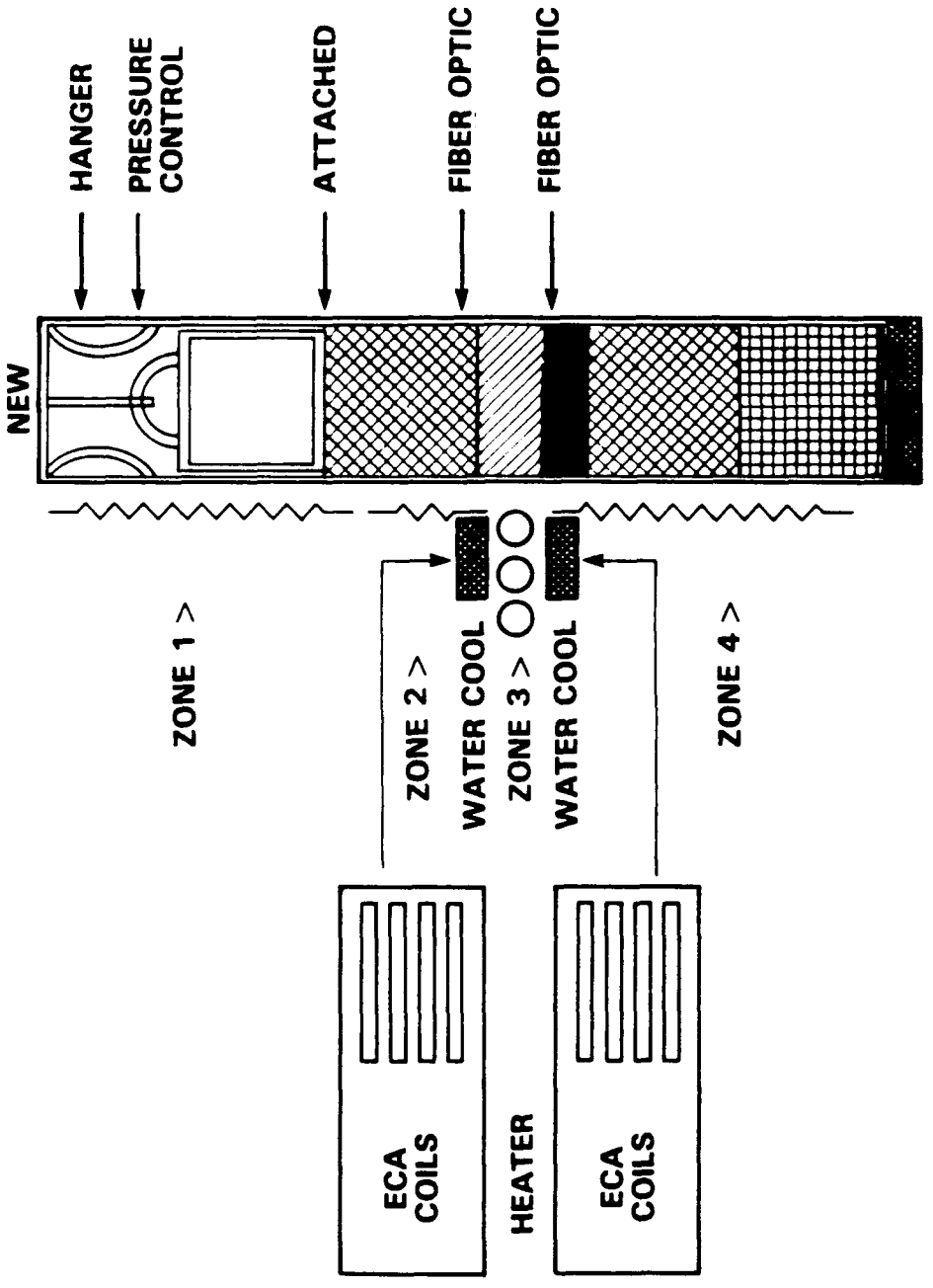


Figure 8. New THM Growth Ampoule Configuration

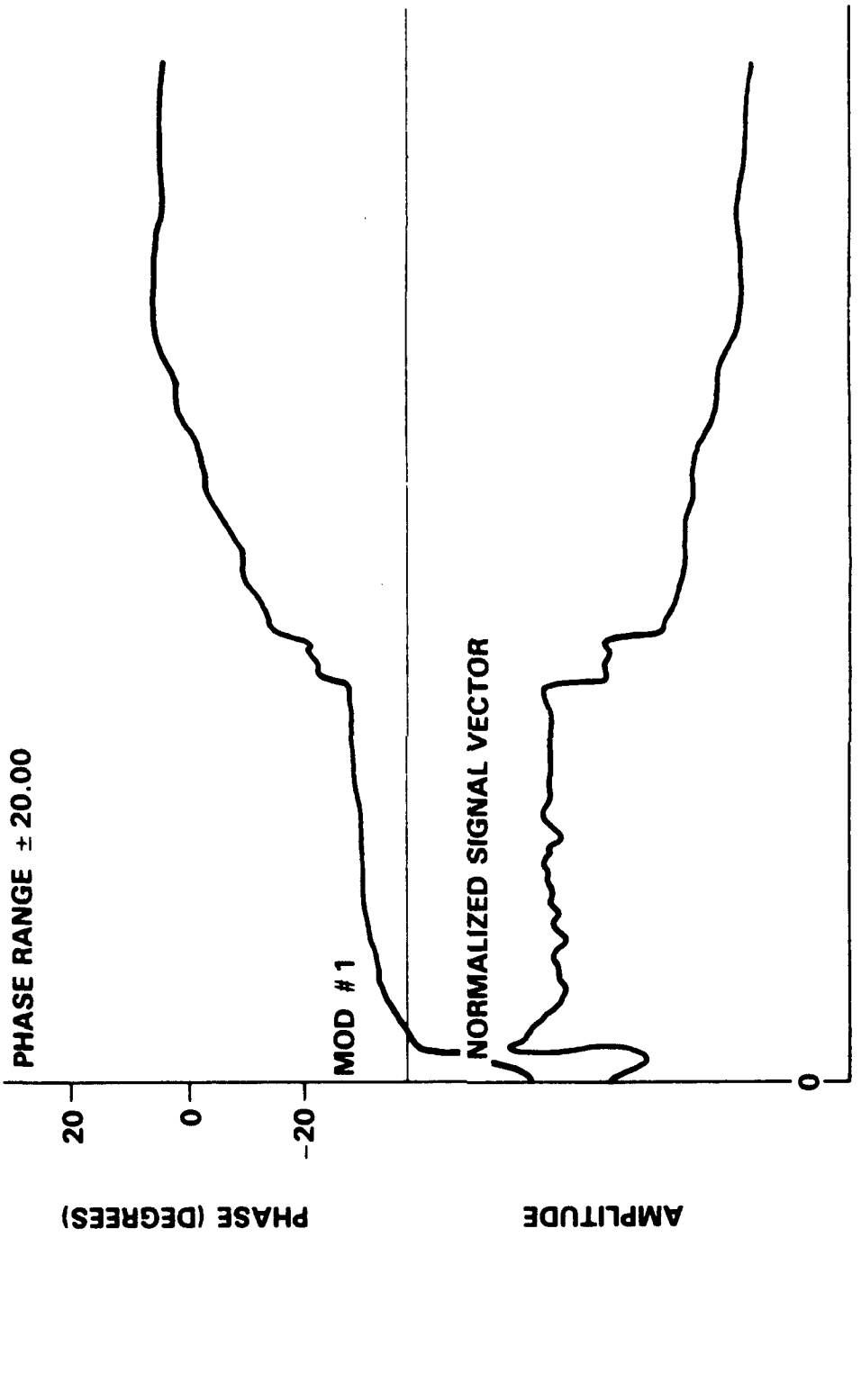
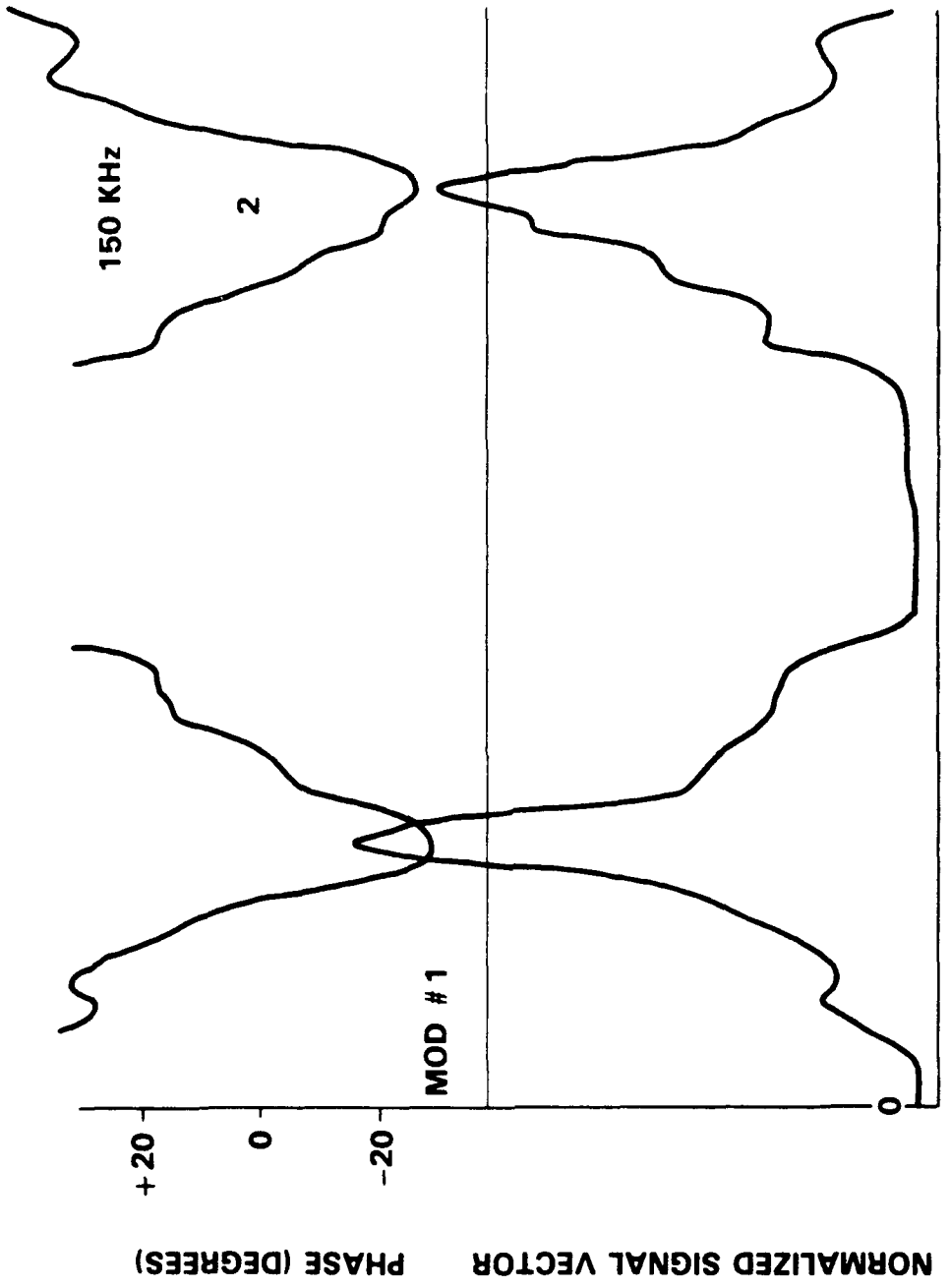


Figure 9. Signal Response From Eddy Current Sensor as HgCdTe Goes Through the Solidification Process



961.13

Figure 10. Signal Response From Eddy Current Sensor as a HgCdTe Ampoule is Passed Through the Sense Coils

These studies will form the basis for interpretation of ECA data obtained in normal system operation. Anticipation is that the ECA data, properly interpreted, will be a primary control signal of the system. The control algorithms themselves can be implemented either in the eddy current equipment or in an external computer control system.

Fiber Optic Thermometer. Precise, repeatable and fast temperature measurement and control are extremely important in the THM growth of HgCdTe materials. The recent advances in Optical Fiber Thermometry (OFT) have allowed measurement and control of the temperature during THM growth with greater range, resolution, repeatability and response than had been possible with thermocouples. Optical fiber thermometers, capable of controlling temperature continuously within 300°C to 3000°C with better than 0.01 C resolution, up to 10 KHz response and complete immunity to electromagnetic interference, are readily available commercially. This advanced OFT technology will be implemented to the THM furnace temperature control, especially in and near the solvent zone. With multiple OFT sensors (or with a single moving OFT sensor), the temperature gradient is mapped out both axially and radially. Close control of the temperature gradient in the solvent zone is critical because it affects the composition gradient within the solvent zone, controls the solid/liquid interface shape which is important in controlling crystallinity, and determines the composition of the solidifying crystal through the phase equilibrium tie line. Precise temperature control using OFT technology will lead to better composition uniformity and better crystallinity in the grown HgCdTe materials.

Hg Pressure Manometer. Due to the volatile nature of Hg at THM growth temperatures it is difficult to obtain a crystal with a precisely specified composition. The concentration of electronic carriers for a given Hg to Cd ratio can be varied by equilibration at temperatures above 200°C under various mercury pressures. Appropriate control of the partial pressure of Hg during the growth and post-growth annealing to obtain a specified composition and to achieve the desired electrical properties is therefore important.

The equilibrium partial pressure of Hg,Cd and Te_2 have been measured extensively over the entire Hg-Cd-Te ternary phase diagram using an optical absorbance technique.[9] The experimental partial pressures obtained were fit fairly well along with phase diagram data using an associated solution model.[10]

A capacitance manometer with high temperature measurement capability will be used first in off-line experiments verifying the mercury partial pressures associated with a high thermal gradient system like the THM ampoule. Partial pressures of mercury in other inert gases may be more measurable than just a mercury partial pressure due to condensation problems in the sensor. Although temperature is the primary pressure control variable, the dynamics of the system may be studied using pressure controlled changes to deplete or enhance the mercury reservoir and/or the solvent zone. An effective model of the relationship between temperature and pressure may make on-line Hg pressure measurement unnecessary. The Hg pressure can then be controlled by the programmed change of the mercury reservoir heater zone temperature set point.

Real-Time Composition Measurements. An effective means to control the composition of the THM crystal during growth would be to measure the composition as a process variable. Photon absorption of gamma rays has been investigated with respect to the mass attenuation for mercury, cadmium and tellurium concentrations in the solvent. Figure 11 shows that ex-

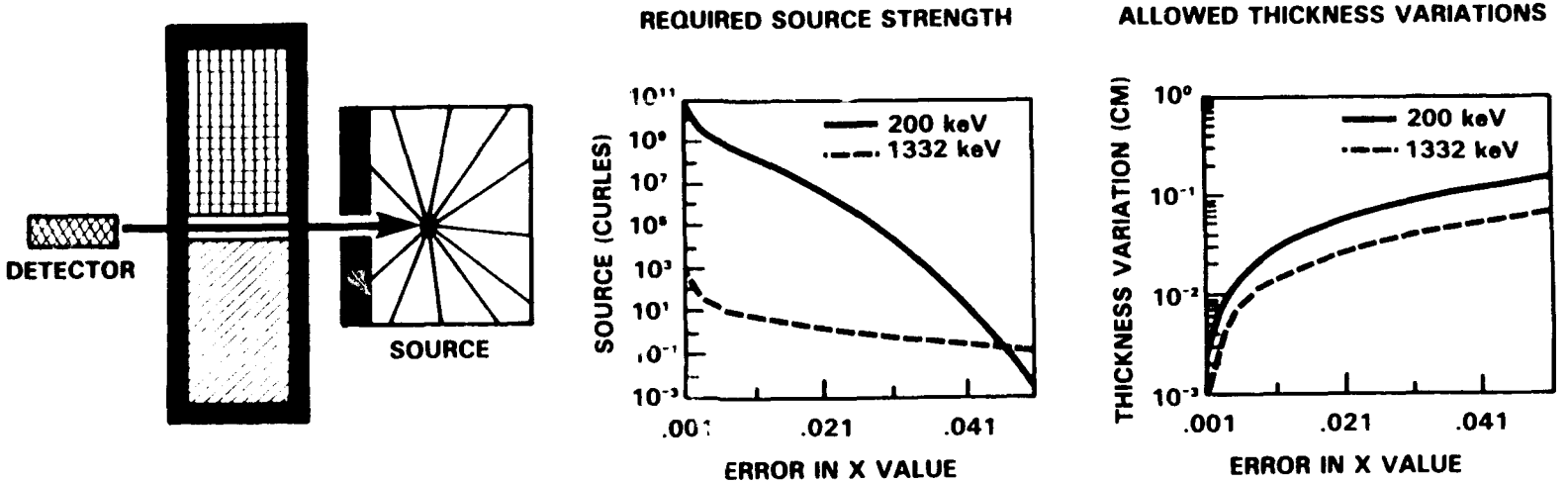


Figure 11. On-Line Determination of THM Composition

NEUTRON PROMPT GAMMA ACTIVATION

1) LITTLE ABSORPTION IN CRUCIBLE
2) INSENSITIVE TO VARIATIONS IN INGOT THICKNESS
3) INSENSITIVE TO CHEMICAL EFFECTS

REACTION	GAMMA-RAY ENERGY	GROSS SECTION	ABUNDANCE
$^{113}Cd(n,g)^{114}Cd$	1661, 559	19910 b	12.3
$^{112}Te(n,g)^{124}Te$	602, 722	406 b	0.9
$^{199}Hg(n,g)^{200}Hg$	368, 1693	2309 b	16.9

961.15

treme source strengths would be required to generate sufficient signal in the detectors. Also variations in the thickness of the solvent due to dimensional changes in the quartz ampoules would limit the relevance of the measurement to changes in composition. Because of the high nuclear cross section of cadmium, the attenuation of neutrons was also considered. However, the cross section for a relatively abundant isotope of mercury is also high and would overwhelm the attempt to measure changes in cadmium concentration in the solvent where it is only one percent. We are continuing to look at prompt gamma reactions for a possible real time on-line composition measurement.

Intelligent Processing of Materials

Approach to Manufacturing Process Control. The theory of optimal control according to Athans and Falb[11] starts with the goals and constraints of the engineering design problem. Once the problem has been defined, the design problem can be approached by directly combining experience, know-how, ingenuity, and the results of experimentation to produce a prototype of the required system. This approach has been taken to date in the THM growth of mercury cadmium telluride. Some capability with large uncontrolled variations has been demonstrated in the process. The thermal modelling carried out under the DARPA-DSO contract[1] has given considerable insight to the problem and presents the opportunity to change the approach to the more standard scientific method of formulating a complete mathematical model of the physical process, the system objectives and the imposed constraints. The adequate mathematical description and formulation of a system design problem is an extremely challenging task. Desirable features like reliability and simplicity are almost impossible to translate into mathematical language.

The state variable description of a dynamic system is one good way of constructing a mathematical model for a physical process. Other means of system analysis are higher order differential equations relating the system inputs to the system outputs or transfer function representation. A state variable description is valid for linear and nonlinear, time-invariant and time-varying systems. The state variable approach is popular because the bulk of modern system theory (i.e., optimal control, stability theory and estimation theory) relies upon state variable representations.

Having formulated the system design problem in terms of a mathematical model, a pencil-and-paper solution to the mathematical version of the design problem or parts of it will produce an idea of the connectivity and sensitivity of the model to parameter variations and unpredictable disturbances. Simulation of the mathematical relationships on a computer will play a vital role in this search for a solution.

The pencil-and-paper design should define the control problem. The essential elements of any control problem are:

1. A mathematical model (system) to be controlled.
2. A desired output of the system.
3. A set of admissible inputs or "controls".
4. A performance or cost functional which measures the effectiveness of a given "control action".

These elements are depicted in Figure 12.

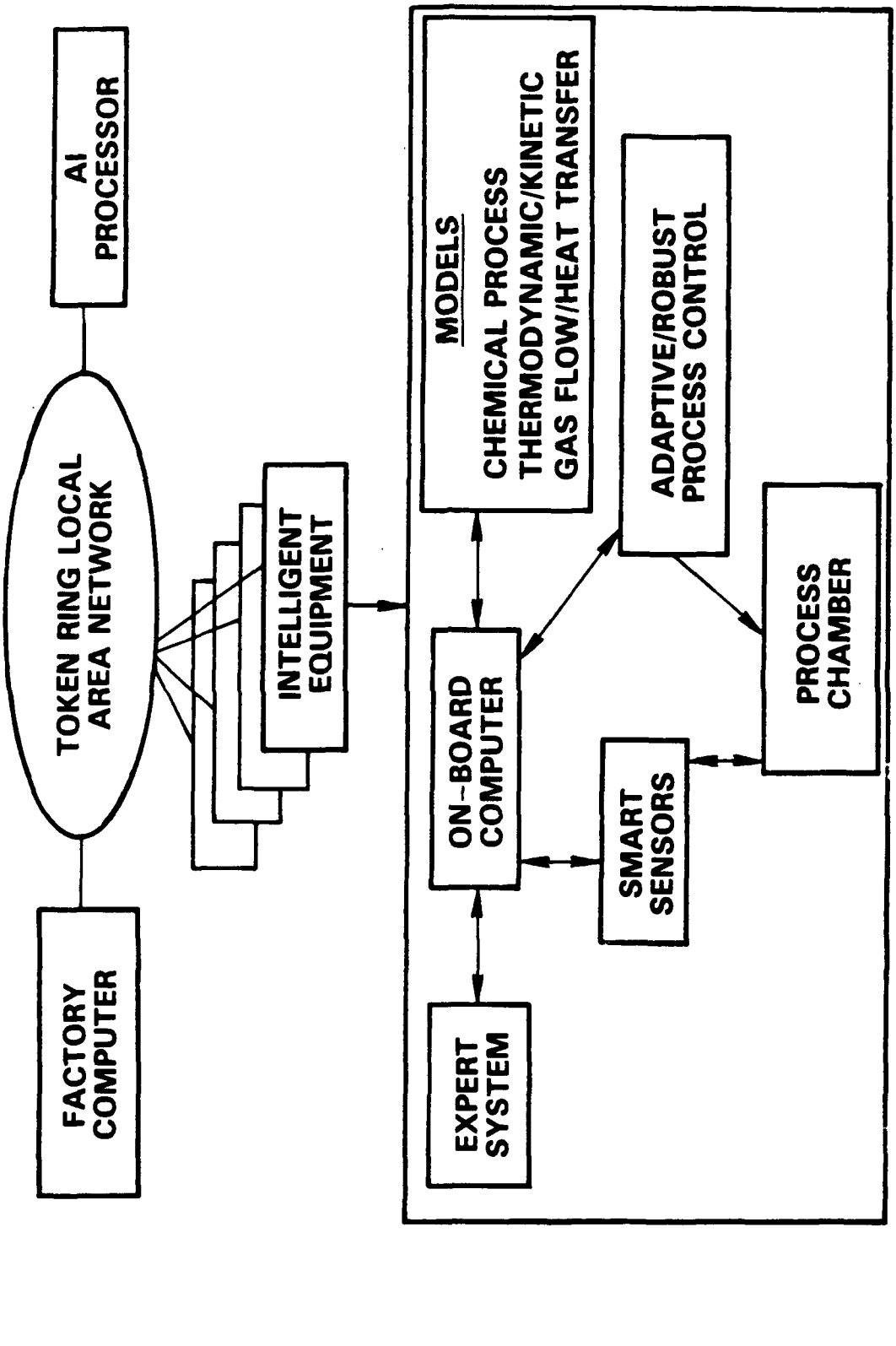


Figure 12. Intelligent Manufacturing Flow Chart

Modern control theory can be viewed as the confluence of three diverse streams: the theory of servomechanisms, the calculus of variations, and the development of the computer. TI has considerable experience in building control systems and robotic machines. The Industrial Systems Division (ISD) has a strategic effort to develop the hardware and software for the needs of its customers. The conceptual ideas will be reduced to models with appropriate state variables and a control gain matrix that adjusts the outputs based on the inputs and the conditions for optimal control will be calculated. Intelligent processing of materials will be achieved even if the control is sub-optimal but effective in establishing a reproducible and economical process.

Much of the THM process control problem has been the lack of definition of the appropriate state variables due to the absence of sensors. The present selection of the new smart sensors is appropriate because of the sensors demonstrated capability for measuring the important parameters of the THM process. The development of data processing methods for dealing with random variables can be traced to Gauss (circa 1800)[12] who invented the technique of deterministic least squares and employed it in a relatively simple measurement problem. He realized the importance of redundant data to eliminate the influence of measurement errors. The Kalman filter is in essence a recursive solution of Gauss' original least squares problem. In addition to optimal control theory there is also a modern theory of optimal estimation that is a computational algorithm that processes measurements to deduce a minimum error estimate of the state of the system utilizing: knowledge of the system and measurement dynamics, assumed statistics of system noise and measurement errors, and initial condition information.[13]

There are three types of estimation problems depending on when the estimate is desired. When the time of the estimate is the time of the last data point, the problem is referred to as filtering; when the time of interest falls within the span of sampled data the term is smoothing; and when the time of interest falls after the last available data the estimate is referred to as prediction. In a multisensor system as proposed, some of the sensors may measure the same quantity of the system. Therefore redundant data may be available to improve the description of the state of the system. Modelling of the sensors themselves is a very large part of modern estimation theory. First the design and evaluation of the "optimal" system behavior is carried out. Then a "suboptimal" system with cost constraints, sensitivity characteristics, computational requirements, and measurement limitations should be brought to mind. Thirdly, the construction and test of a prototype measurement system allows changes and adjustments as warranted.

The heuristics of artificial intelligence (AI) has been applied to similar control problems only recently with some success. Dolins, et. al. have demonstrated an AI approach to "Monitoring and Diagnosis of Plasma Etch Processes" at TI using a signal to symbol transformer and a set of generic rules that analyzes the system with respect to time and compares the durations to detect problems using other process specific rules.[14] These rules were established by the process engineer as criteria for judging the acceptable or unacceptable performance of the system. The time constraints on many systems limits this application of rule based systems for real time process control applications. Since the THM process is a very slow and very critical process, it should be a good candidate for optimal real time intelligent processing of materials.

The TI approach to the control problem of reaction, cognition, and reflection is implemented with the TI565 programmable logic controller (reaction) which is supervised by the TISTAR cell controller (cognition) that also acts as the operator's interface to the factory and is advised by an as yet to be defined AI engine (reflection) of the TI Explorer family. Both the TI565 and the TISTAR systems are intended for the factory control environment with optical isolation of outputs and proven field installations in large chemical and food processing plants. This equipment is installed in our THM pilot line without the proposed smart sensors that should bring our process under control. Another option under consideration is the ESP module that is a complete personal computer intended for installation in the I/O base of the TI565 programmable logic controller. This could be used for the integration of the smart sensors or even possibly as the AI engine for determining the updated coefficients in the multivariable control gain matrix for the real time optimal process control. This architecture would be a state-of-the-art demonstration that would set the stage for other activities for the intelligent processing of materials.

Acknowedgements

The author would like to thank the following for their contributions:

Bobbie Baird
Kent Carson
Jerry Chang
Peng-Heng Chang
Luigi Colombo
Pok-Kai Liao
James Robinson
Bob Smythe
A.J. Syllaios
Glenn Westphal
Mike Williams

References

1. Chang et al, to be published J. Crystal Growth.

2. Don W. Shaw, "Numerical Simulation of HgCdTe Liquid Phase Epitaxy," Journal of Crystal Growth, (62)247, 1983.

3. R.F. Brebrick, Ching-Hua Su, and Pok-Kai Liao, "Associated Solution Model for Ga-In-Sb and Hg-Cd-Te," Semiconductors and Semimetals, edited by R.K. Willardson and A.C. Beer, Vol. 19: Ch. 3, Academic Press 1983.

4. C.V. Dodd and W.E. Deeds, Journal of Applied Physics 39 (1968), pp. 2829-2838.

5. J.P. Wallace, D.C. Kunerth, and R.M. Siegfried, "An Eddy Current Study of Casting", Eddy Current Characterization of Materials and Structures ASTM STP 722, George Birnbaum and George Free, Eds., American Society for Testing and Materials, 1981, pp. 173-186.

6. C.V. Dodd, C.C. Cheng, and W.E. Deeds, Journal of Applied Physics 45 (1074), pp. 638-847.

7. J.A. Stefani, J.K. Tien, K.S. Choe, J.P. Wallace, Journal of Crystal Growth 88 (1988), pp. 30-38.

8. R.M. Siegfried, J.P. Wallace, G.A. Boser, and D.C. Kunerth, "Quantitative Models for Eddy Current Analysis of Metal Solidification", Nondestructive Evaluation: Microstructural Characterization and Reliability Strategies, Otto Buck and Stanley M. Wolf, Eds., The Metallurgical Society of AIME, Warrendale, PA, 1981, pp. 223-252.

9. Ph.D Dissertation, Pok-Kai Liao, Marquette University, Milwaukee, WI, 1983.

10. R.F. Brebrick, Ching-Hua Su, and Pok-Kai Liao, Semimetals and Semiconduc-tors, Vol. 19: Ch. 3, Edited by R.K. Willardson and A.C. Beer, 1983.

11. Athans, Michael and Falb, Peter, "Optimal Control", McGraw Hill, 1966, pp. 1-14.

12. Gauss, K.F., "Theoria Motus", 1809; Theory of the Motion of the Heavenly Bodies About the Sun in Conic Sections, Dover, New York, 1963.

13. Gelb, Arthur, "Applied Optimal Estimation", The M.I.T. Press, 1974, pp. 1- 5.

14. Dolins, S.B., Srivastava, A., Flinchbaugh, B.E., "Monitoring and Diagnosis of Plasma Etch Processes", IEEE Transactions on Semiconductor Manufacturing, Vol. 1, No. 1, Feb. 1988, pp. 23-27.